

Method for Correcting Molecular Weight from Gel Permeation Chromatography. II. Long-Chain Branching Correction of Low-Density Polyethylenes

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Synopsis

Direct measurement of intrinsic viscosity on gel permeation chromatography effluent was performed with use of an automatic viscometer in order to determine molecular characteristics of branched polymers. In analyzing the viscosity data, the instrumental spreading was considered. Results obtained from three low-density and one high-density polyethylene were compared with those obtained by such other methods as osmometer, light scattering, and column elution fractionation.

INTRODUCTION

Recently, various attempts to characterize branched polymers using GPC chromatograms have been made by many investigators. Drott^{1,2} first proposed a skillful method by combining GPC chromatogram with intrinsic viscosity. This method assumes that the long-chain branching frequency λ is independent of molecular weight. However, recent work³⁻⁵ on the branching of low-density polyethylenes has suggested that λ is not constant, but varies appreciably with molecular weight. This molecular weight dependence differs for every samples. It is, therefore, required to determine the dependence for each sample in order to calculate real molecular characteristics of low-density polyethylenes. This requires much labor and time. Combination of GPC and an automatic viscometer^{6,7} really serves this purpose. In the combination, the solution collected in the syphon is directly introduced into an automatic viscometer being sunk in a thermostat regulated at constant temperature ($\pm 0.01^\circ\text{C}$). The capillary diameter and the capillar length of the viscometer should be selected so as to have a flow time shorter than the time required for the subsequent filling of the syphon.

According to the method established by Grubisic-Gallot et al.,⁷ the intrinsic viscosity of the fraction between syphon counts i and $i + 1$ is expressed by

$$[\eta]_i = \frac{t_i - t_0}{t_0} \times \frac{S}{S_i} \times \frac{V}{m} \quad (1)$$

where t_0 and t_i are the flow times of solvent and the solution collected between

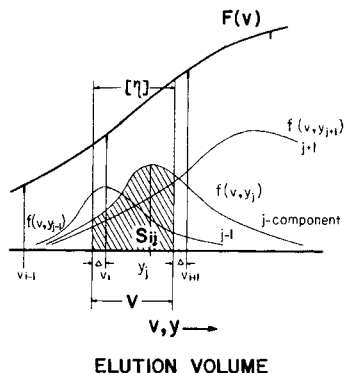


Fig. 1. Schematic expression of method 1.

syphon counts i and $i + 1$, respectively; S is the total area of the observed chromatogram, S_i is the area corresponding to the syphon volume between syphon counts i and $i + 1$; V is the syphon volume; and m is the amount of the polymer injected. As can be easily understood, the intrinsic viscosity is an average one corresponding to a difference in elution volume of about 5 ml (syphon volume) and, in addition, is affected by the instrumental spreading. It should be corrected in some way.⁸ In this paper, we present two methods for estimating real intrinsic viscosity corresponding to corrected chromatogram in order to determine the real molecular characteristics of branched polymers from the GPC viscometer.

METHODS FOR CORRECTING INTRINSIC VISCOSITY

Method 1

As reported in previous papers,^{9,10} GPC chromatograms can be expressed as resultant of many instrumental spread chromatograms for monodisperse components. This can be extended to intrinsic viscosity data. That is, $[\eta]_i$ corresponding to the fraction between the syphon counts i and $i + 1$ can be expressed as follows:

$$\begin{aligned}
 [\eta]_i &= [\eta]_{i_1} \times S_{i_1} + [\eta]_{i_2} \times S_{i_2} + \dots + [\eta]_{i_j} \times S_{i_j} + \dots \\
 &= \sum_{j=1}^n [\eta]_{i_j} \times S_{i_j}
 \end{aligned}
 \quad (2)$$

Figure 1 schematically represents the theory. In eq. (2), S_{i_j} is the weight ratio of the j th component in the fraction between syphon counts i and $i + 1$; $[\eta]_{i_j}$ is the intrinsic viscosity of the component. Then,

$$[\eta]_{1j} = [\eta]_{2j} = \dots = [\eta]_{ij} = \dots \quad (3)$$

S_{i_j} can be expressed as

$$S_{i_j} = \frac{\int_{v_i - \Delta}^{v_i - \Delta + V} f(v, y_j) dv}{\sum_{j=1}^n \int_{v_i - \Delta}^{v_i - \Delta + V} f(v, y_j) dv}
 \quad (4)$$

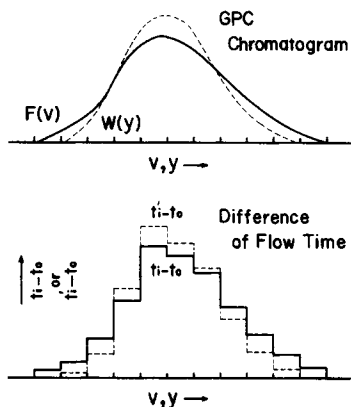


Fig. 2. Schematic expression of method 2.

where

$$f(v, y_j) = W(y_j) \times G(v, y_j) \quad (5)$$

v is the elution volume; v_i and y_j are the elution volumes corresponding to the syphon count i and to the chromatogram peak for the j th component, respectively; $G(v, y_j)$ is the chromatogram for unit input (1 mg) of the j th component—the instrumental spreading function; $W(y_j)$ is the amount (in mg) of the j th component (it is related to the corrected chromatogram and determined by the method previously reported by us¹⁰); and Δ is the dead volume between the differential refractometer and the syphon.

Equation (4) can be solved by Simpson's rule. $[\eta]_{ij}$ can be determined from eq. (2) by linear programming when $[\eta]_i$ and S_{ij} are employed as input data. The molecular weight of the j th component (M_j) can be calculated with use of the universal calibration curve, which is valid for low-density polyethylene.¹²

The long-chain branching frequency of the j th component (λ_j) is determined by the following equation reported by Zimm and Stockmayer,¹¹ because it is natural to assume that almost all low-density polyethylenes are random trifunctional branched polymers with branches of random length:

$$g_j = \left[\left(1 + \frac{M_j \times \lambda_j}{7} \right)^{1/2} + \frac{4 \times M_j \times \lambda_j}{9\pi} \right]^{-1/2} \quad (6)$$

TABLE I
Characteristics of Whole Polymers

Sample	$\langle M \rangle_n \times 10^{-4a}$	$\langle M \rangle_w \times 10^{-4b}$	$[\eta]^c$	$-\text{CH}_3/1000 \text{ C}^d$
A	2.20	27.8	0.981	30.9
B	2.49	41.3	0.975	30.0
C	2.40	22.4	0.914	29.5
NBS1475	1.83	5.2	1.010	1.5

^a Osmometer, in tetralin at 105°C.

^b Light scattering, in α -chloronaphthalene at 125°C.

^c Capillary viscometer, in trichlorobenzene at 130°C.

^d Infrared spectroscopy.

where

$$\lambda_j = \frac{M_j}{n_j}$$

$$g_j^\epsilon = \frac{[\eta]_{b0j}}{[\eta]_{l0j}}$$

$[\eta]_{b0j}$ and $[\eta]_{l0j}$ are the unperturbed intrinsic viscosity of branched and linear polymers at M_j , respectively; and n_j is the number of long-chain branch points in the j th component. The molecular weight for whole polymers can be calculated by the following equations:⁹

$$\langle M \rangle_n = \frac{\sum_{j=1}^n G_j \times W(y_j) \times M_j}{\sum_{j=1}^n G_j \times W(y_j) / M_j} \quad (7)$$

$$\langle M \rangle_w = \frac{\sum_{j=1}^n G_j \times W(y_j) \times M_j}{\sum_{j=1}^n G_j \times W(y_j)} \quad (8)$$

$$[\eta] = \frac{K \times \sum_{j=1}^n G_j \times W(y_j) \times M_j^\alpha}{\sum_{j=1}^n G_j \times W(y_j)} \quad (9)$$

where K and α are constants in the Mark-Houwink equation, and G_j is the weight coefficient for the Gaussian quadrature.

Method 2

Figure 2 schematically represents the theory. The difference of the flow time corrected for the instrumental spreading may be expressed as follows:

$$t_i' - t_0 = (t_i - t_0) \times \frac{W(y_{a_i})}{F(v_{a_i})} \quad (10)$$

where t_i and t_i' are the observed and the corrected flow times of the solution, respectively; and $F(v)$ and $W(y)$ are the normalized observed and the corrected chromatograms. Therefore, from eqs. (1) and (10), the corrected intrinsic viscosity is expressed by

TABLE II
Molecular Characteristics Obtained According to Method

Sample	Method 1			Method 2			Drott method		
	$\langle M \rangle_n$ $\times 10^{-4}$	$\langle M \rangle_w$ $\times 10^{-4}$	$[\eta]$	$\langle M \rangle_n$ $\times 10^{-4}$	$\langle M \rangle_w$ $\times 10^{-4}$	$[\eta]$	$\langle M \rangle_n$ $\times 10^{-4}$	$\langle M \rangle_w$ $\times 10^{-4}$	$[\eta]$
A	1.61	30.2	0.827	1.54	29.9	0.893	1.60	622	0.882
B	1.90	72.1	0.946	1.77	55.4	1.029	1.36	3000	0.974
C	2.43	52.4	0.887	2.23	29.2	0.945	1.72	432	0.911
NBS1475	1.94	5.78	0.949	1.88	5.50	0.973	1.58	6.90	1.01

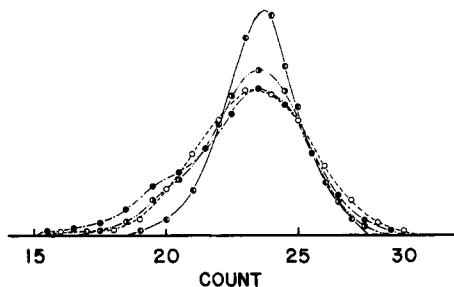


Fig. 3. GPC chromatograms: (○) A; (●) B; (◐) C; (◑) NBS 1475.

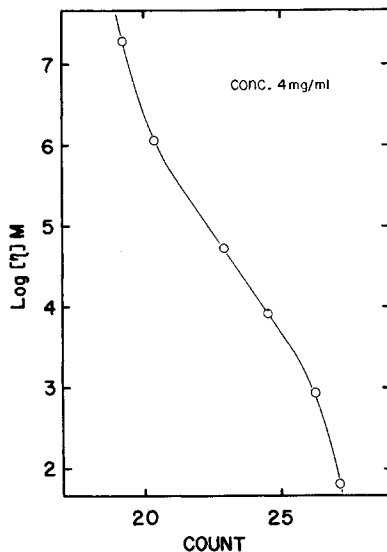


Fig. 4. Universal calibration curve.

$$[\eta]_{i'}' = \frac{(t_i - t_0) \times \frac{W(y_{a_i})}{F(v_{a_i})}}{t_0} \times \frac{S}{S_i} \times \frac{V}{m} \tag{11}$$

where v_{a_i} and y_{a_i} are the average elution volumes for the fraction collected between syphon counts i and $i + 1$, which are defined as the values corresponding to the abscissa of the vertical line cutting $F(v)$ and $W(y)$ between two successive counts into two equal areas.

Now, as it is possible to assume S_i as $W(y_{a_i})$, $S = \sum W(y_{a_i}) = 1$, eq. (11) can be rewritten to

$$[\eta]_{i'}' = \frac{t_i - t_0}{t_0} \times \frac{1}{F(v_{a_i})} \times \frac{V}{m} \tag{12}$$

The molecular characteristics are calculated from eqs. (6)–(9), as well as method 1.

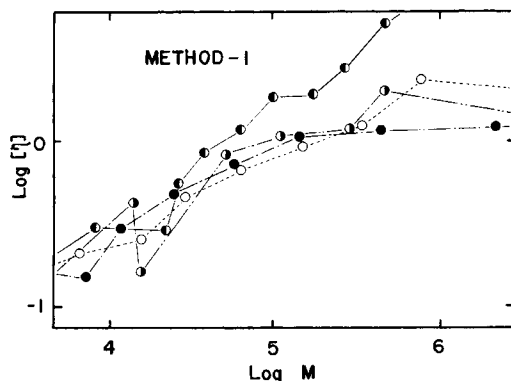


Fig. 5. Relation between intrinsic viscosity and molecular weight, method 1: (O) A; (●) B; (◐) C; (◑) NBS 1475.

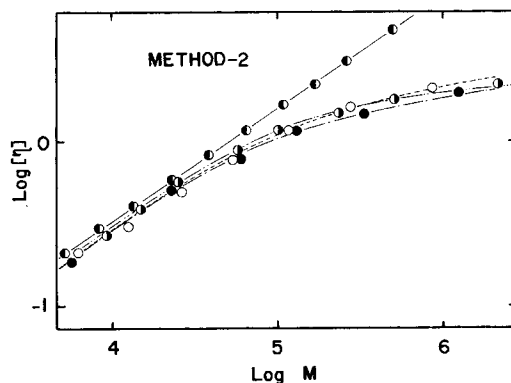


Fig. 6. Relation between intrinsic viscosity and molecular weight, method 2: (O) A; (●) B; (◐) C; (◑) NBS 1475.

EXPERIMENTAL

Samples

Three commercial low-density polyethylenes (A, B, and C), one high-density polyethylene (NBS 1475), and the fractions prepared from A were examined. Fractionation was performed by the column elution method. These samples were characterized by measurements of $\langle M \rangle_w$ by light scattering, of $\langle M \rangle_n$ by osmometry, and of $[\eta]$ by capillary viscometer. The results are listed in Table I.

Gel Permeation Chromatography

The GPC measurements were performed on a Waters Model 200 under the following conditions: column combination, 10^3 , 10^4 , 10^5 , 10^6 Å; solvent, 1,2,4-trichlorobenzene; flow rate, 1 ml/min; temperature, 130°C ; input solution con-

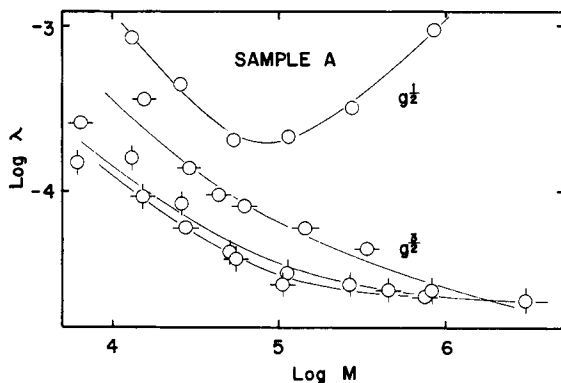


Fig. 7. Molecular weight dependence of λ for sample A: (O) method 1, $g^{3/2}$; (\odot) method 2, $g^{3/2}$; (\ominus) method 2, $g^{1/2}$; (\oplus) fractionation.

centration, 4 mg/ml; injection time, 2 min. The calibration was performed by use of Pressure Chemical's monodisperse polystyrenes.

Automatic Viscometer

Capillary diameter, 0.420 mm; capillary length, 100 mm; upper bulb volume, 3.0 cc; lower bulb volume, 2.0 cc; temperature, $130.00 \pm 0.01^\circ\text{C}$. The kinetic energy correction was performed by use of pure benzene.¹³

RESULTS AND DISCUSSION

The results calculated by methods 1 and 2 are listed in Table II, compared with those by the Drott method. It is seen from Tables I and II that the values of $\langle M \rangle_w$ calculated by method 2 are very close to those measured by light scattering, but in other methods they are larger; especially in the Drott method they are unreasonably large. We think that this is because of the absence of the instrumental spreading correction. When the chromatogram is broad and the calibration curve has a steep slope, the instrumental spreading correction is absolutely required. Figures 3 and 4 show the chromatograms and the universal calibration curve in these experiments. The values of $\langle M \rangle_n$ calculated by GPC are smaller than those measured by osmometry. This is caused by permeation of low molecular weight species in membrane osmometric measurement.

The agreement of $[\eta]$ with the experimental data in the Drott method stands to reason. Figures 5 and 6 show the relation between $\log [\eta]$ and $\log M$. The scattering of the data calculated by method 1 is mainly attributable to the experimental error in the automatic viscometer measurements. In the regions of high and low molecular weight, the flow time difference $t_i - t_0$ and the chromatogram area S_i are so small that it is difficult to exactly determine $[\eta]_i$ from eqs. (1) and (2) by linear programming.

Method 2 is better than method 1 and the Drott method from the standpoint of the agreement with the values measured by osmometry, light scattering, viscometry, and fractionation. Method 2 can be further improved by reducing the syphon volume to avoid the mixing of fractionated polymer species in the syphon.

In determining λ_j from eq. (6), the ratio of intrinsic viscosity for branched

polyethylenes to linear polyethylenes with the same molecular weight under theta conditions is assumed to be consistent with that under nontheta conditions (TCB, 130°C).^{14,15} Figure 7 shows the molecular weight dependence of λ .

This dependence is in accord with the result found by Williamson and Cervenka;⁵ that is, λ is not constant throughout the molecular weight range in both case of $\epsilon = \frac{1}{2}$ and $\frac{3}{2}$. The increase in λ with decreasing molecular weight in the region of low molecular weight must be attributed to the effect of short-chain branching.

From the results in this study, the following can be concluded:

1. The molecular weight dependence of λ must be considered in calculating molecular characteristics of low-density polyethylenes from GPC chromatograms.
2. Satisfactory methods for correcting the instrumental spreading on intrinsic viscosity data and for calculating molecular characteristics from GPC viscometer data have been developed.

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